

WORK AND HEAT

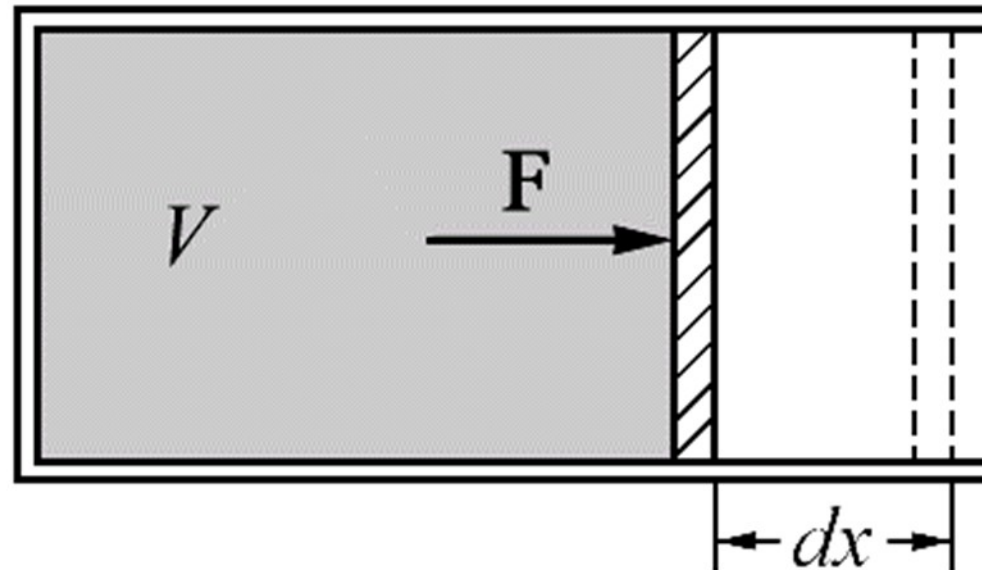
A thermodynamic system can possess both internal and mechanical energy, and different systems can exchange these types of energy. The exchange of **mechanical energy** is characterized by **work done** A , and the exchange of **internal energy** by the amount of transferred **heat** Q . **Mechanical energy** can be converted into **thermal energy** and vice versa.

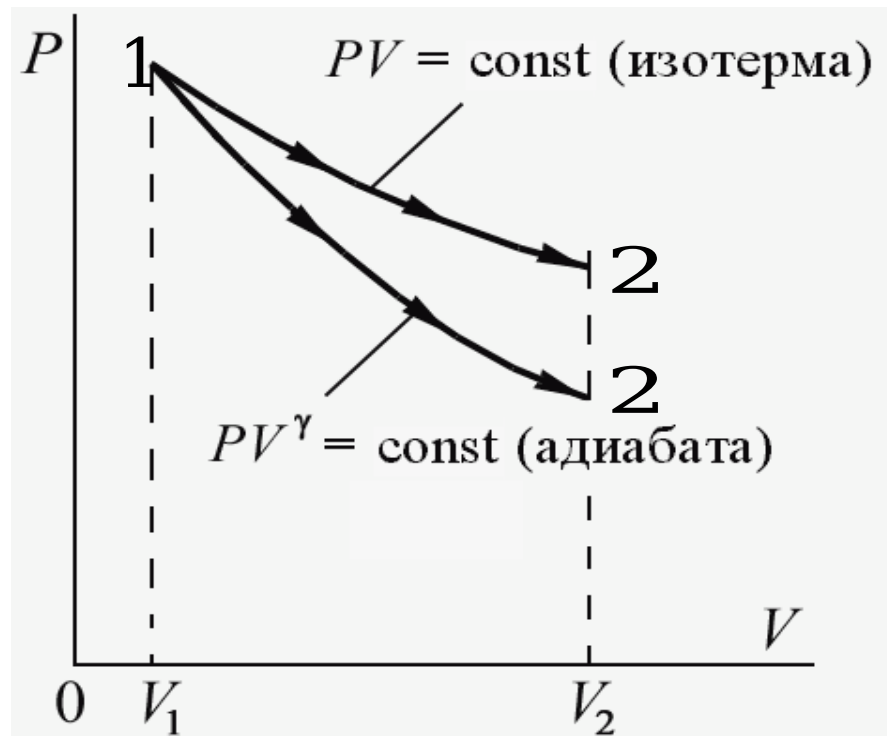
WORK

The work performed by the system with an infinitely small change in the volume of the system dV is equal to:

$$\delta A = Fdx = PSdx = PdV$$

- Here $P = F / S$ is the gas pressure in the vessel; S is the area of the piston; $dV = Sdx$ - change in vessel volume when moving the piston by dx

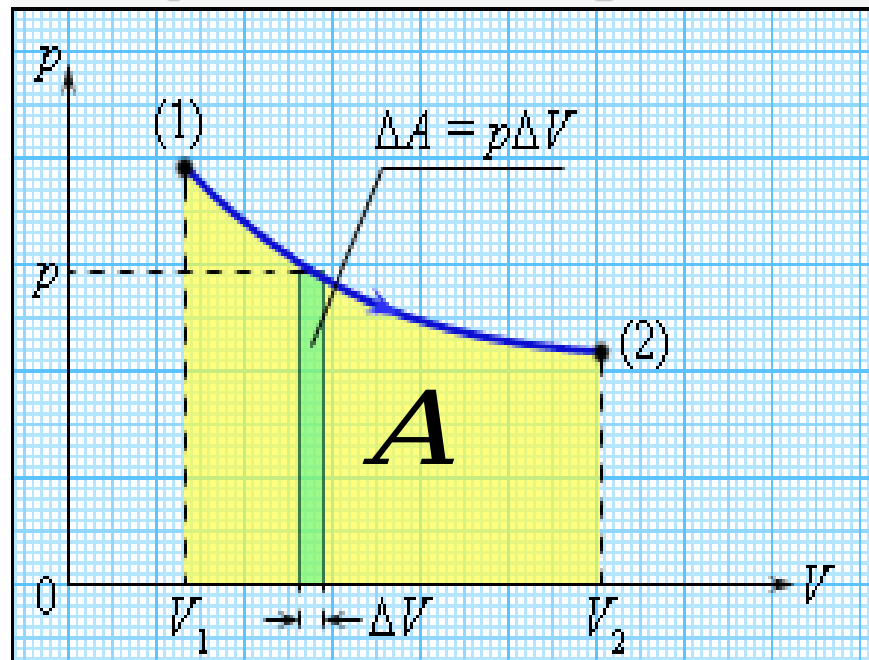




In the transition from state 1 to state 2 (a finite change in volume), the pressure can

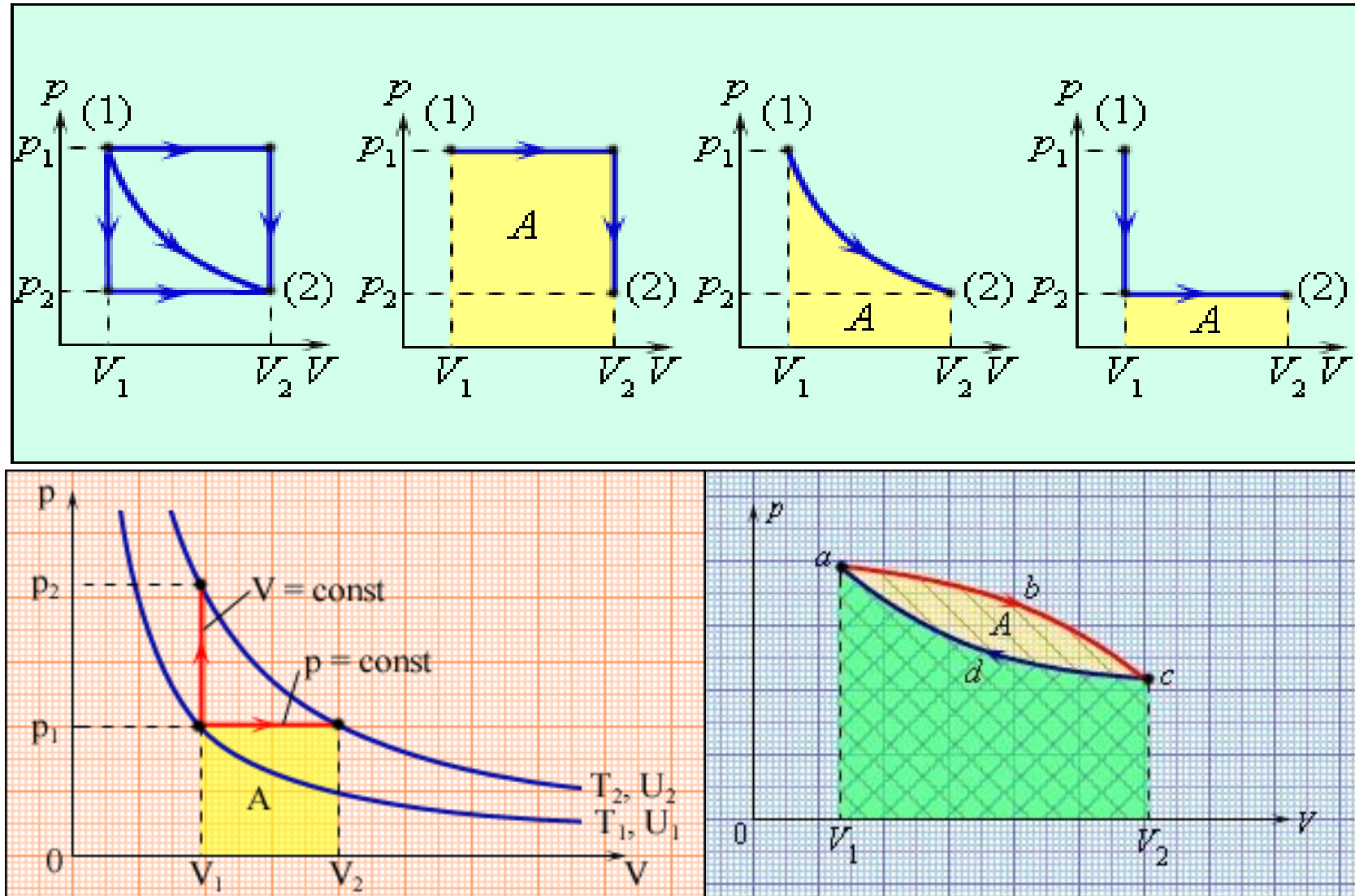
vary V_2

$$A = \int_{V_1}^{V_2} p dV$$



The geometric interpretation of the integral is the area under the curve 1 - 2. The area depends on the type of curve. Therefore, macroscopic work is not a function of the state, but a

The work done on a gas as it is taken from an initial state to a final state depends on the path between these states.



Heat and Internal Energy

Heat is defined as the transfer of energy across the boundary of a system due to a temperature difference between the system and its surroundings.

The amount of heat Q , represents the energy that is transferred from one body to another when they contact (directly or through the 3rd body) or by radiation. The amount of heat (heat lot) is a measure of the change in the internal energy of a system during heat transfer: heat conductivity, thermal radiation, convection

(heat transfer, caught by the difference temperatures in different

The first law of thermodynamics

- The first law (the first principle) of thermodynamics represents a special case of the law of conservation and transformation of energy in application to thermal phenomena.
- This is a postulate that can not be logically deduced or proved, and its validity is confirmed by the results of the experiment.
- There are various formulations of the first law of thermodynamics; they are all equivalent.

The first law of thermodynamics

- The law of conservation of energy in application to thermodynamic processes is one of such expressions of the first law of thermodynamics.
- Different forms of energy transfer into each other in strictly equivalent quantities
- Internal energy of any isolated system remains constant, despite the processes taking place in it.

The first law of thermodynamics

- Work is also one of the forms of energy transformation, therefore, it is impossible to create a perpetual mobile (first perpetuum mobile), i.e. such a periodically operating machine, which would produce work without the expenditure of energy from outside.
- One of the main formulations of the first law is the following: the heat communicated to the system in any process is spent on incrementing the internal energy of the system and the work done.

$$Q = \Delta U - A$$

The law of conservation of energy for a small change in the state of the system will look like:

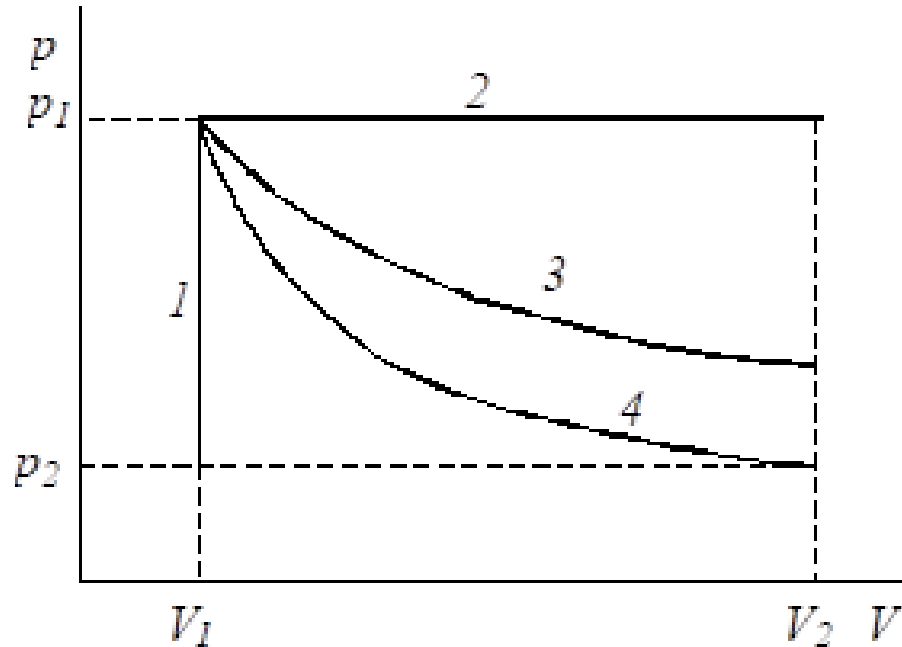
$$\delta Q = dU - \delta A$$

- U is the function of the state of the system; dU is its total differential, and δQ and δA are not such and their increments are not full differentials.

- The heat Q and work A depend on how the transition from state 1 to state 2 is made (isochoric, adiabatic), and the internal energy U is independent.
- At the same time, it cannot be said that the system has a value of heat and work defined for a given state.
- The amount of heat Q is expressed in the same units as work and energy, i.e. in joules $[Q] = J$.

The first law of thermodynamics

- Depending on the conditions of the operation, there are different types of processes



- Dependence of p - V for different processes: 1 - isochoric; 2 - isobaric; 3 - isothermal; 4-adiabatic

Process Terminology

- Adiabatic –no heat transferred
- Isothermal –constant temperature
- Isobaric –constant pressure
- Isochoric –constant volume

Adiabatic Process

- An adiabatic process transfers no heat therefore $Q = 0$
- $\Delta U = Q - W$
- When a system expands adiabatically, W is positive (the system does work) so ΔU is negative.
- When a system compresses adiabatically, W is negative (work is done on the system) so ΔU is positive.

ADIABATIC PROCESS

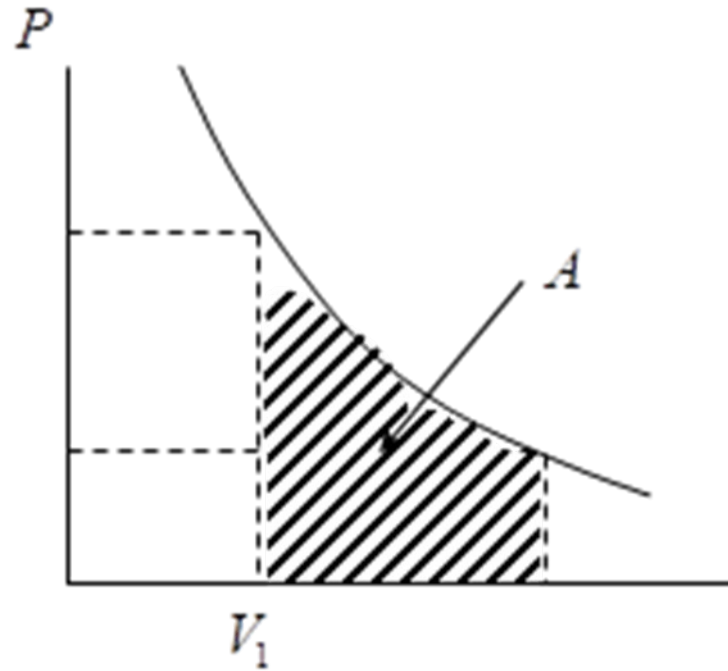
- In the adiabatic process, the system does not exchange heat with the environment ($Q = 0$), so
- $A = -\Delta U$;
- $A = c_v (T_1 - T_2)$;
- $A = (p_1 V_1 - p_2 V_2)/(\gamma - 1)$.
- where $\gamma = c_p / c_v$ is the ratio of isobaric and isochoric heat capacities; for an ideal gas, $c_p = c_v + R$ and $c_v = R/(\gamma - 1)$. The pressure and volume in the initial and final states are related by the adiabatic equation:
 - $p_1 V_1^\gamma = p_2 V_2^\gamma$
- Therefore, the work of the adiabatic process can also be calculated from the equation:
- $A = \frac{RT_1}{\gamma - 1} \left(1 - \frac{V_1^{\gamma-1}}{V_2^{\gamma-1}} \right)$

Isothermal Process

- An isothermal process is a constant temperature process. Any heat flow into or out of the system must be slow enough to maintain thermal equilibrium
- For ideal gases, if ΔT is zero, $\Delta U = 0$
- Therefore, $Q = W$
- Any energy entering the system (Q) must leave as work (W)

ISOTHERMAL PROCESS

- $T = \text{const}$



ISOTHERMAL PROCESS

- In the isothermal process ($T = \text{const}$) per one mole of gas

$$A = - \int_{V_1}^{V_2} \frac{RT}{V} dV = - RT \ln \frac{V_2}{V_1} = RT \ln \frac{p_1}{p_2} .$$

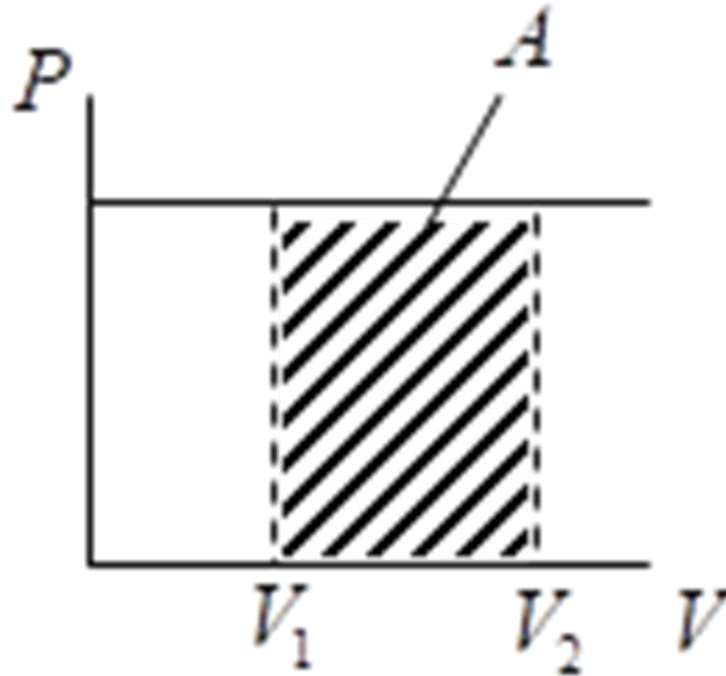
- Since in the isothermal process for an ideal gas $\Delta U = 0$, to $Q_p = -A$, i.e. The heat supplied to the system is completely transformed into work.

Isobaric Process

- An isobaric process is a constant pressure process. ΔU , W , and Q are generally non-zero, but calculating the work done by an ideal gas is straightforward
 - $W = P \cdot \Delta V$
- Water boiling in a saucepan is an example of an isobar process

ISOBARIC PROCESS

- $p = \text{const}$ $Q = du + p dv$ $Q = \Delta H$



ISOBARIC PROCESS

- In the isobaric process ($p = \text{const}$), the work of expansion A and for one mole of an ideal gas
$$A = - p(V_2 - V_1) = - p\Delta V$$
- Then
$$Q_p = \Delta U + p\Delta V = (U_2 - U_1) + p(V_2 - V_1) =$$
- $= (U_2 + pV_2) - (U_1 + pV_1) = H_2 - H_1 = \Delta H,$
- where $H = (U + pV)$ is called the enthalpy of the system. Enthalpy, like internal energy, is a function of the state, and its changes do not depend on the path of the process.

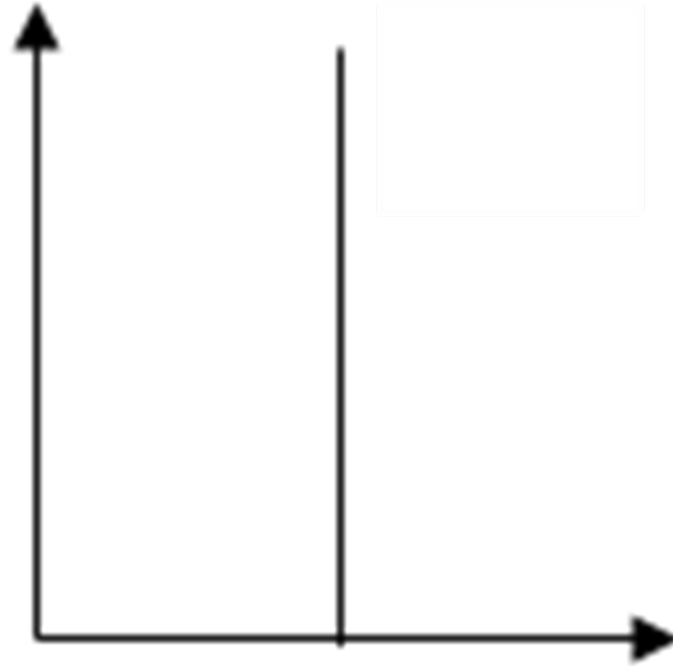
Isochoric Process

- An isochoric process is a constant volume process. When the volume of a system doesn't change, it will do no work on its surroundings. $W = 0$
 - $\Delta U = Q$
- Heating gas in a closed container is an isochoric process

ISOCHORIC PROCESS

- $dV = 0$

$$\delta Q = dU$$



ISOCHORIC PROCESS

- In an isochoric process, the volume of the system does not change ($dV = 0$), therefore, the work of expansion is zero and
- $\delta Q_V = dU$, a $(dU/dT)_V = (\delta Q/dT)_V = c_V$
- where c_V is the specific heat at constant volume; for a monoatomic ideal gas it is equal to $3R/2$. It follows that
- $dU = c_V dT$ or $\Delta U = c_V \Delta T$
- Heat of the isochoric process
- $Q_V = U_2 - U_1 = \Delta U$.
- For an ideal gas equation is valid not only for isochoric, but for any process in which the volume and pressure vary arbitrarily.

The heat capacity of the ideal
gas

The heat capacity of the body is characterized by the amount of heat required to heat this body by one degree

$$C = \frac{\Delta Q}{dT}$$

Heat capacity dimension: $[C] = \text{J/K}$.

Heat capacity is an indefinite quantity; therefore, the concepts of specific and molar heat capacity are used.

Specific heat capacity C_{sp} - is the amount of heat required to heat a unit mass of a substance by 1 degree

$$[C_{уд}] = \text{Дж}/(\text{кг} \cdot \text{К}). \quad C_{sp} = \frac{\Delta Q}{m \cdot dT}.$$

For gases it is convenient to use the molar heat capacity C_{μ} the amount of heat required to heat 1 mole of gas per 1 degree

$$C_{\square} = C_{sp} \square$$

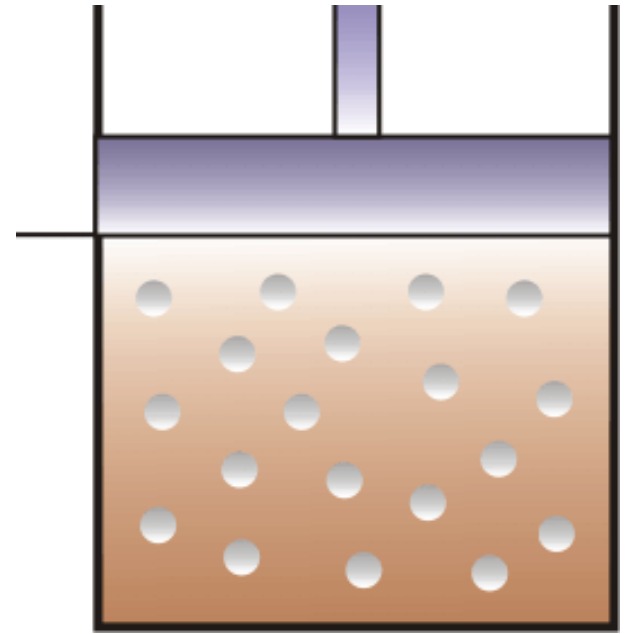
$$[C_{\mu}] = \text{J}/(\text{mole} \cdot \text{K}).$$

The heat capacity of the thermodynamic system depends on how the state of the system changes when heated.

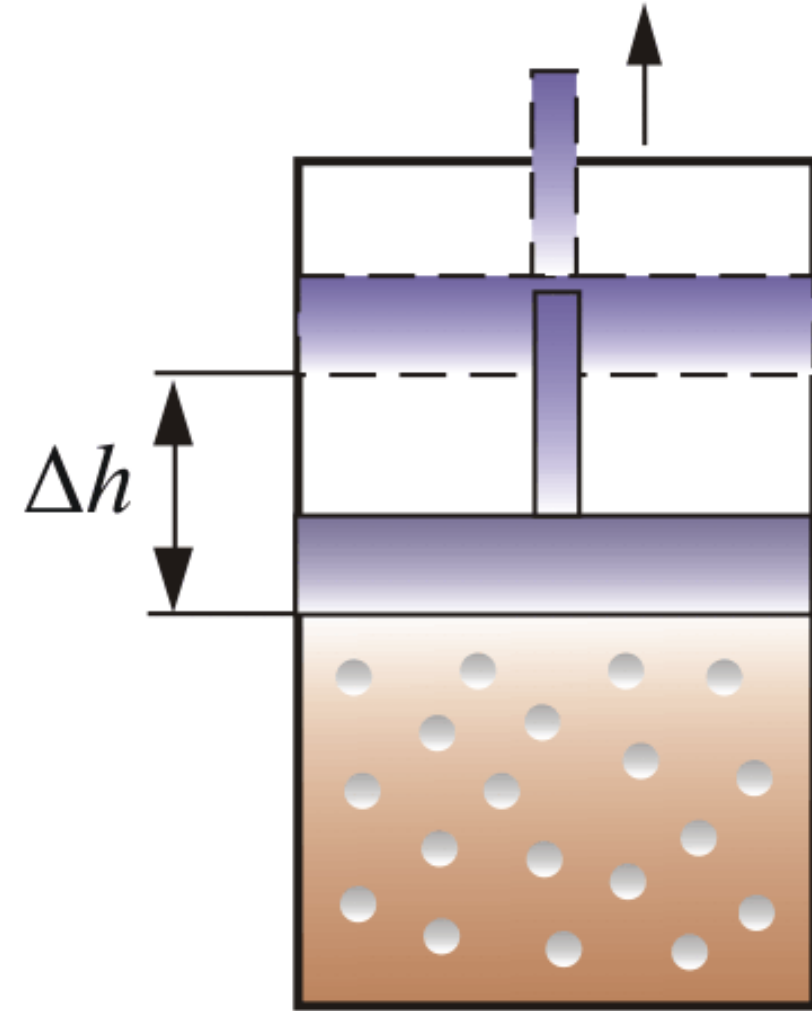
If the gas is heated at a constant volume, then all the supplied heat goes to heating the gas, that is, a change in its internal energy.

Heat capacity at constant volume C_V

$$C_V = \left(\frac{\Delta Q}{dT} \right)_V = \left(\frac{dU}{dT} \right)_V$$



C_p - heat capacity at constant pressure.
If the gas is heated at a constant pressure P in the vessel with the piston, then the piston rises to a certain height h , that is, the gas does the work.



Therefore, the conducted heat is expended both on heating and on performance of work. Hence it is clear that

$$C_p > C_v$$

So, the conducted heat and specific heat depend on how the heat transfer is carried out. Therefore, Q and C are not state functions. The values of C_p and C_v turn out to be connected by simple relations.

During the isobaric process, in addition to increasing the internal energy, gas is performed work):

$$\Delta Q_P = dU_{\square} + P dV_{\square}$$

$$C_P = \frac{\Delta Q_P}{dT} = \frac{dU_{\square}}{dT} + P \frac{dV_{\square}}{dT}$$

(for 1 mole)

$$PV_{\square} = RT.$$

From the basic equation of the molecular-kinetic theory for 1 mol: In the isobaric process, $P = \text{const.}$ Then we get:

$$C_P = C_V + R$$

This is Robert Meyer's equation for one mole of gas.

$$C_p = C_v + R$$

It follows from it that the physical meaning of the universal gas constant is that R - is numerically equal to the work performed by one mole of gas when heated by one degree during the isobaric process.

Using this relation, Robert Meyer in 1842 calculated the mechanical equivalent of heat:
 $1 \text{ cal} = 4.19 \text{ J}$.

For ν moles:

$$C_p = C_v + \nu R$$

In the general case

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

since the internal energy U can depend only on temperature.

In the case of 1 mole of an ideal gas, the formula is corrected. internal energy:

$$dU_{\square} = C_V dT$$

Из этого следует, что для 1 моля:

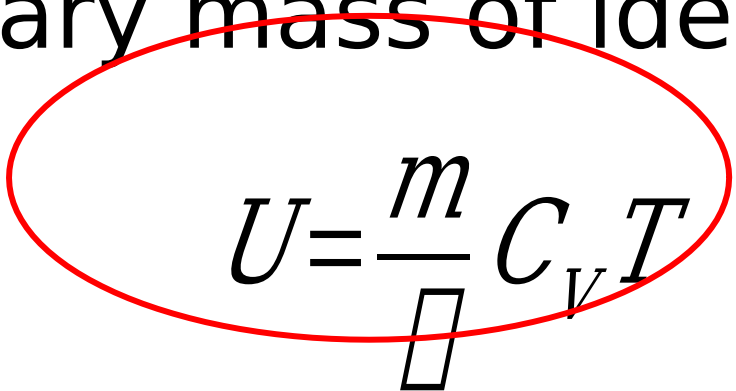
$$U_{\square} = \int_0^T C_V dT = C_V T$$

$$U_{\square} = C_V T$$

The internal energy of an ideal gas is only a function of temperature (and does not depend on V , P and the like), therefore, the formula is valid for any process (for 1 mole).

$$U_{\square} = C_V T$$

For an arbitrary mass of ideal gas:


$$U = \frac{m}{\square} C_V T$$

The internal energy of one mole of an ideal monatomic gas is equal to:

$$U_{\square} = N_A \frac{3}{2} kT = \frac{3}{2} RT$$

$$U_{\square} = \frac{3}{2} RT$$

$$C_V = \left(\frac{dU}{dT} \right)_V = \frac{3}{2} R = 12,5 \frac{\text{Дж}}{\text{моль} \cdot \text{К}},$$

- the molar heat capacity at a constant volume of C_V is a constant value, it does not depend on temperature.

The internal energy of one mole of an ideal gas with i degrees of freedom is equal to:

$$U_{\square} = \frac{i}{2} RT$$

$$C_V = \left(\frac{dU}{dT} \right)_V = \frac{i}{2} R$$

the molar heat capacity at a constant volume of C_V is a constant value, it does not depend on temperature.

Given the physical meaning of R for isobaric processes, we can write:

$$dQ_p = dU + R dT$$

(for one mole) From here for the monatomic: $C_p = \frac{5}{2}R + R = \frac{7}{2}R$
 Then, constant pressure molar heat capacity for monatomic gases:

$$C_p = \frac{5}{2}R = 20,8 \frac{\text{Дж}}{\text{моль} \cdot \text{K}}$$

For one mole of ideal gas:

$$C_P = \frac{i}{2} R + R = \frac{i+2}{2} R$$

Adiabatic constant (Poisson's ratio) for ideal gas:

$$\frac{C_P}{C_V} = \frac{i+2}{i} = \gamma$$

For a monatomic ideal gas ($i = 3$):

$$\gamma = \frac{20,8}{12,5} = 1,67$$

HEAT CAPACITY

- The total heat capacity of a system is the amount of heat required to raise the temperature of the system for one degree.
- it is an extensive quantity, it is more convenient to use the heat capacity per unit quantity of matter. Depending on this, a specific (by 1 g or 1 kg of mass) and a mole (per mole) heat capacity are distinguished.
- The heat capacity depends on the nature of the substance and also on the temperature,
- so there are average heat capacity in a given temperature range (from T_1 to T_2) and the true heat capacity

HEAT CAPACITY

- The average heat capacity approaches the true with decreasing temperature interval, when $(T_2 - T_1) \rightarrow 0$.
- The relationship between the average and true specific heats can be established on the basis that the amount of heat necessary for heating the system from T_1 to T_2 is a strictly defined quantity. It does not depend on the calculation method, therefore (at constant pressure)

$$Q_p = \tau_p(T_2 - T_1) = \int_{T_1}^{T_2} c_p dT$$

$$\bar{c}_p = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} c_p dT$$

Kirchhoff's Equation

- As $(dH/dT)_p = c_p$
- $(d\Delta H_p/dT)_p = \nu_3 (dH_C/dT)_p + \nu_4 (dH_D/dT)_p + \dots - \nu_1 (dH_A/dT)_p - \nu_2 (dH_B/dT)_p$
- Or in general
- $(d\Delta H_p/dT)_p = \Sigma(\nu_k c_{p,k})_{\text{prod}} - \Sigma(\nu_i c_{p,i})_{\text{init}} \equiv \Delta c_p,$
- Integrating this equation within the temperature range from T1 to T2, we can obtain:

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta c_p dT$$